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"PASSIVE VIBRATION DAMPING MATERIALS: PIEZOELECTRIC CERAMIC COMPOSITES FOR VIBRATION DAMPING APPLICATION"

ANNUAL REPORT

Period: January 1991 to December 1991

DEPARTMENT OF THE NAVY

OFFICE OF NAVAL RESEARCH, CODE 1513: RAR

GRANT NO: N00014-90-J-1540

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June 1992

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ABSTRACT

Based on the theory and experiments developed in the first year's research work, the use of piezoelectric composites has been explored for application as large area structural composite material with built-in damping.

Two parallel efforts have been carried out in this second year effort. One is to demonstrate piezoelectric composite damping using prototype macroscopic damping elements made from piezoelectric ceramic tubes available on the market, embedded in a polymer or fiber-reinforced polymer and shunted with external resistors. The other part of the effort is to fabricate fine fibers of PZT using sol-gel technology, with an eye toward future piezoelectric fiber-reinforced polymer composites. From these amorphous fibers, PZT fibers of 50-150 μm diameter and length of up to 1 cm have been fabricated. After heat treatment at 700°C the fibers were fully crystallized in the perovskite structure.

1. INTRODUCTION

This project has been originated in January 1990 under ONR's Acoustic Damping Materials Accelerated Research Initiative. The unique feature of our effort in the program, which focused initially on both metals and polymer composites, is the use of ferroelectric composites to produce damping with controllable frequency characteristics. In the first year, we have focused on the use of a piezoelectric ceramic material, namely, a lead zirconate titanate (PZT), and composite incorporating PZT (1). The theory was developed and fundamental experiments on piezoelectric damping were carried out. These experiments showed electrical to thermal energy conversion occurs due to dissipation of the electric charge, developed by the active piezoelectric ceramic elements as thermal energy by I^2R heating in a shunting resistance element. Extremely high damping efficiency (mechanical loss factor of 0.25) coupled with a high elastic modulus of 70 GPa was achieved using an electrical resonance technique. However, the samples were too small to directly measure the low frequency acoustic damping and, furthermore, were not suitable for, as well as too difficult to produce as, large area materials for structural damping applications.

Therefore, one objective in 1991 was to fabricate composite samples using commercially available PZT tubes for the eventual scale into the processing of structural composite materials. A second objective was to find a way to make fine ($\leq$ 100 μm) PZT fibers. Progress on PZT fiber formation by the sol-gel method has been made, which will make fabrication of large area piezoelectrically damped composite materials feasible in the future.

A PZT two-tube module with a hard epoxy matrix was successfully fabricated to test the effect of the PZT tube's piezoelectric damping. Since then till the end of the project year, the method to produce longitudinally poled PZT tubes embedded in a glass fiber reinforced epoxy using prepreg tape has been studied. Several attempts failed to produce a long sample, due to the difficulties in the processing technique.

Modeling and design optimization was initiated by Professor G. Lesieutre at the Aerospace Engineering Department (outside of the funding for 1991). This modeling is included in 1991 project year funding.

The effort of fabricating sol-gel derived PZT fiber has progressed to the point that dense fibers with a diameter of 50 to 150 μm have been achieved. The length of the fiber after firing is still short (1 to 10 mm) due to the difficulty in continuous fiber spinning and thus inhomogeneous gel fiber. Further study on the control of binder burnout and sintering of these fiber samples are required to produce higher quality fibers. In addition, the development of electrical measurement and poling methods are still needed.

2. PZT TUBE/POLYMER COMPOSITES

2.1. Two tube module

PZT 5H tubes with an outside diameter of 1.24 mm and length of 100 mm were provided from Morgan Matroc, Inc., Vernitron Division. Poling along the tube axis was performed, since k_{33} is the most effective electro-mechanical coupling coefficient to use (1). In order to verify the use of these tubes for damping applications, the simplest form of a 1-3 composite that is the two tube module embedded in epoxy was made and tested. By connecting an external resistance, reduction in the conductance peak height and increase in calculated mechanical $\tan\delta$ indicated that the mechanical damping was performing as predicted. A concern is that the effective coupling (k_{eff}) of the two tube module was 0.33, whereas that of a single tube after poling was 0.66. Although some degree of loss in the coupling coefficient was expected due to the polymer interactions, it is important to maintain the high k_{eff}. Detailed experimental procedure and results are attached in Appendix A.

2.2. Glass fiber reinforced epoxy matrix

One type of structural materials having the advantages of high strength and light weight is fiber reinforced polymers. Studies of the vibration damping properties of fiber reinforced polymers have been carried out elsewhere (2). Since piezoelectric ceramic damping composites require a high modulus of rigidity, non-conductive matrix, glass fiber reinforced epoxy seemed to be the best choice of matrix material. A sample of Scotchply Type SP-250E (3M) was obtained, and the design of the composite along with the processing study is currently continued. The use of a so-called "smart press," which is a small scale autoclave where the pressure application is strictly uniaxial, is required for fabricating PZT tube/glass fiber reinforced epoxy samples. Fine tuning of the processing temperature and pressure are necessary since it lies between the required prepreg processing temperature and pressure and the PZT depoling temperature and fracture pressure.

2.3. Modeling and optimization

The ability to tailor the frequency-dependence of damping is important in practical structural applications. The theory of multiple resistively-shunted piezoelectric elements has been worked out by Lesieutre and co-workers at the Aerospace Engineering Department with the collaboration of the Materials Research Laboratory. The paper summarizing this work is attached as Appendix B.

3. PZT SOL-GEL DERIVED FIBERS

The need for very fine (<150μm) piezoelectric fibers to construct the 1-3 damping composite structure, which grew out of the first year of this contract, has led us to examine a variety of methods. Because of the volatility of lead at processing temperatures, PZT fibers cannot be fabricated by the melt process in the same way as are silica fibers, for example. The sol-gel process with metal alkoxides as precursors has been extensively studied for the fabrication of ceramic materials of various forms such as ultra fine powders and thin films. Based on the rich resource of sol-gel chemistry we have in the Materials Research Laboratory at Penn State University currently being applied to the area of PZT thin film work, we decided to capitalize on this asset. The fabrication of lead titanate (PT) and PZT fibers has been performed from viscous

spinnable solution prepared by sol-gel processing of alkoxide precursors. Detailed information on this process is in the attached published paper in Appendix C.

A study on niobium doped PZT fiber formation to obtain higher coupling coefficient is currently performed in addition to further optimization of the processing.

4. PUBLISHED JOURNAL PAPERS, PRESENTATION IN PROFESSIONAL MEETINGS

— U. Selvaraj, A.V. Prasadarao, S. Komarneni, K. Brooks, and S. Kurtz, "Sol-gel processing of $Pb(Zr_{0.52}Ti_{0.48})O_3$ fibers," J. Mater. Res. 7 (1992) 992-996.

— S. Yoshikawa, Q.C. Xu, A.R. Ramachandran, S.K. Kurtz, "Passive Piezoelectric Damping Composites," ASM International Materials Week '91, 21-24 Oct. 1991, Cincinnati, OH (Abstract is attached in Appendix D).

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2. NASA Tech Briefs, MFS-27228, August 1989.

APPENDIX A

Summary of Preparation and Testing of 2-Tube Passive Damping Module (Vernitron PZT 5H Tubes)

I. Preparation of Module

A. Electroding for Poling
B. Poling
C. Electroding for Damping Module
D. Application of Epoxy

II. Testing of Completed Module

A. Spectrum Analysis
B. Conductance (G) vs. Frequency (f) Data Summary, with and without External Resistance

A. Calculation of External Resistance Required

August 13, 1991
Keith G. Brooks

cc: Dr. Kurtz
Dr. Xu
S. Yoshikawa

I. Preparation of Damping Module

A. Electroding for Poling

The electrode configuration used to pole the PZT tube samples was as illustrated in Figure 1. A silver/glass electroding compound was applied to the tubes to form circumferential electrodes approximately 1 mm in width and 1 cm center to center separation. 10 electrodes were applied to each tube. Heat treatment of electrodes at 800°C for 30 minutes followed application.

B. Poling Procedure

Tubes were poled individually using a fixture designed specifically for this purpose. The tubes were suspended in a silicon oil bath held at 80°C and poled for 10 minutes with an applied field of approximately 10 kV/cm. After poling, the coupling coefficient was calculated from resonance frequency data. The calculated k_{33} was 0.66. This compares with a value of 0.75 as provided by Vernitron. Figure 2 shows the resonance spectrum of a poled sample. The fundamental resonant and antiresonant frequencies were 15.45 and 19.29 kHz, respectively. The electrode configuration used for the resonance measurement is diagrammed in Figure 3.

C. Electroding for Damping Module

In preparation for electroding, poled PZT tubes were soaked in 1,1,1 trichloroethane for 24 hours to clean and remove silicon oil from surfaces. Fine silver wire was attached to the fired on silver electrodes using a two part conductive adhesive silver epoxy (Allied E-solder 3021) which can be cured at room temperature. The two tube module was constructed as shown in Figure 4.

D. Application of Epoxy

A small quantity of black epoxy was mixed (20 grams part A, 5 grams part B). The damping module was suspended horizontally by the electrode wires and the epoxy was applied with a spatula. The insides of the tubes were not filled with epoxy due to high viscosity. The epoxy was cured at room temperature for 24 hours followed by a heat treatment at 60-65°C for 45 minutes.

II. Testing of Completed Module

A. Spectrum Analysis

Spectrum analysis was carried out using the electrode configuration shown in Figure 5. Spectral data is shown in Figure 6. From this data a coupling coefficient for the module was calculated, for the fundamental resonance at 3350 Hz. A value of keff = 0.33 was obtained.

B. Conductance (G) versus frequency (f) data, with and without External Resistance connected

The circuit used for this analysis is diagrammed in Figure 7. For measurements without external resistors, electrodes 5 and 6 were attached to the impedance analyzer. Frequencies were scanned between 0.05 and 10 kHz at 10 or 20 Hz intervals. External resistances of 1, 4.7, 10 14.7 Mohm were used. G vs. f data is shown in Figure 8a-f. An initial estimate of the resistance required was 18.2 M-ohm, as per calculation below:

Estimation of External Resistance Requirement:

$$R_{ext} = \frac{\ell}{\omega \varepsilon \varepsilon_o Se}$$

ℓ	=	length of tube segment = 0.009 m
ω	=	angular frequency = $(2\pi)\cdot 4061$
ε	=	dielectric constant = 3400
ε_o	=	permittivity of free space = 8.85×10^{-12}
Se	=	effective electrode area = 7.8×10^{-7}
R	=	18 MΩ

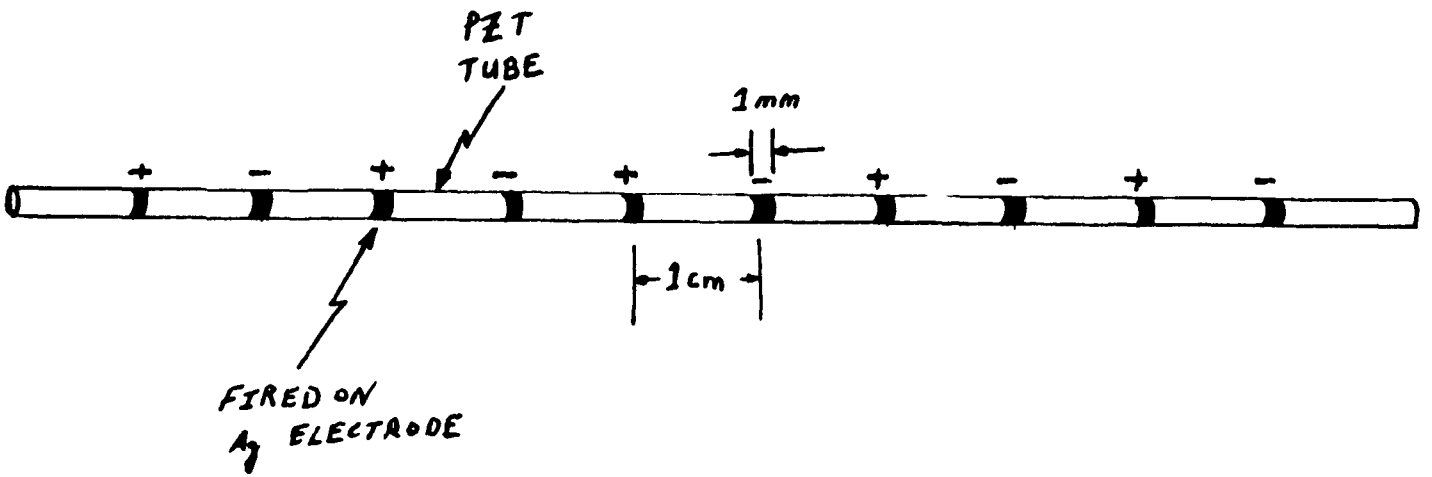
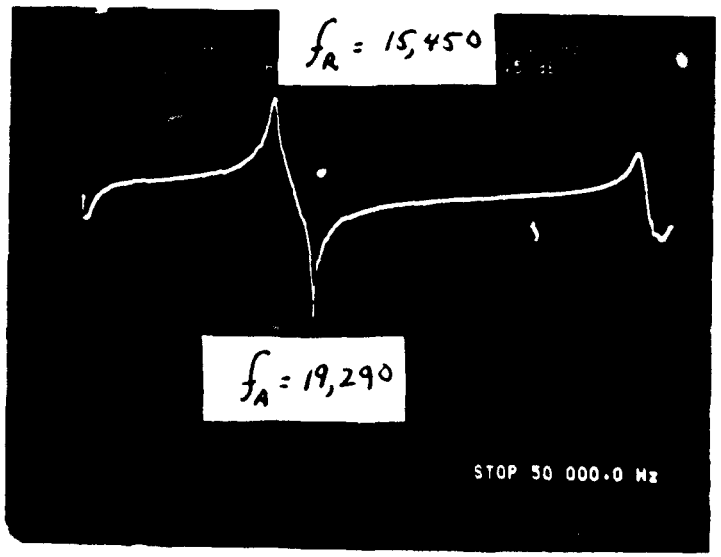


Fig.1 Electrode configuration for poling.

$$K_{33} = \sqrt{\frac{\pi^2}{8}\left(1 - \frac{f_R^2}{f_A^2}\right)}$$

$$K_{33} = 0.66$$



Y

f(Hz)

Fig.2 Piezoelectric resonance after poling (10kV/cm, 10min, 80C).

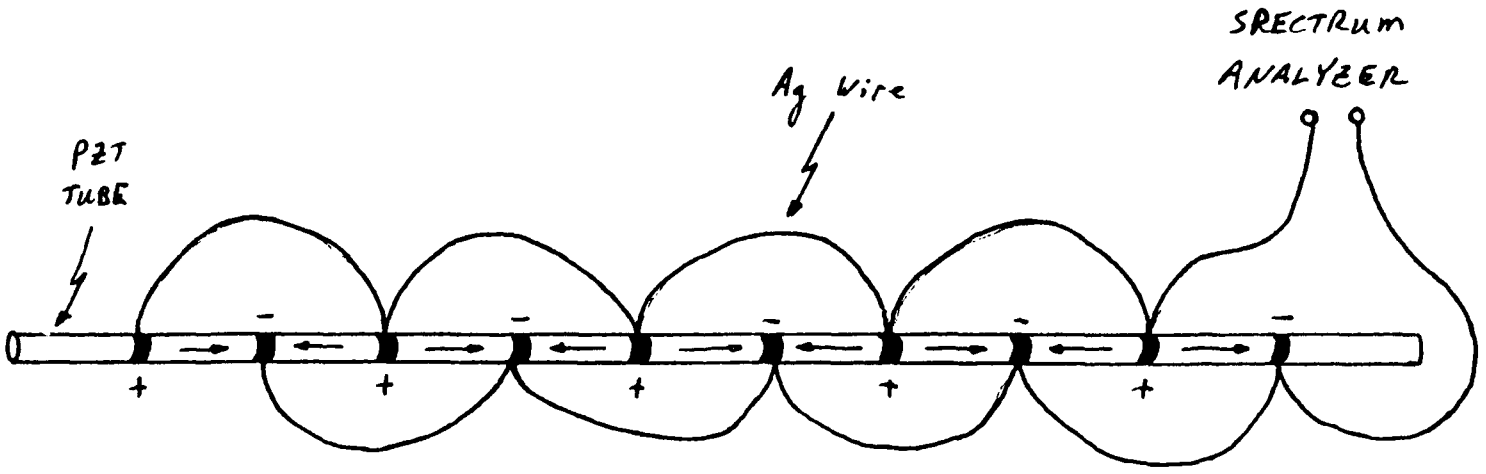
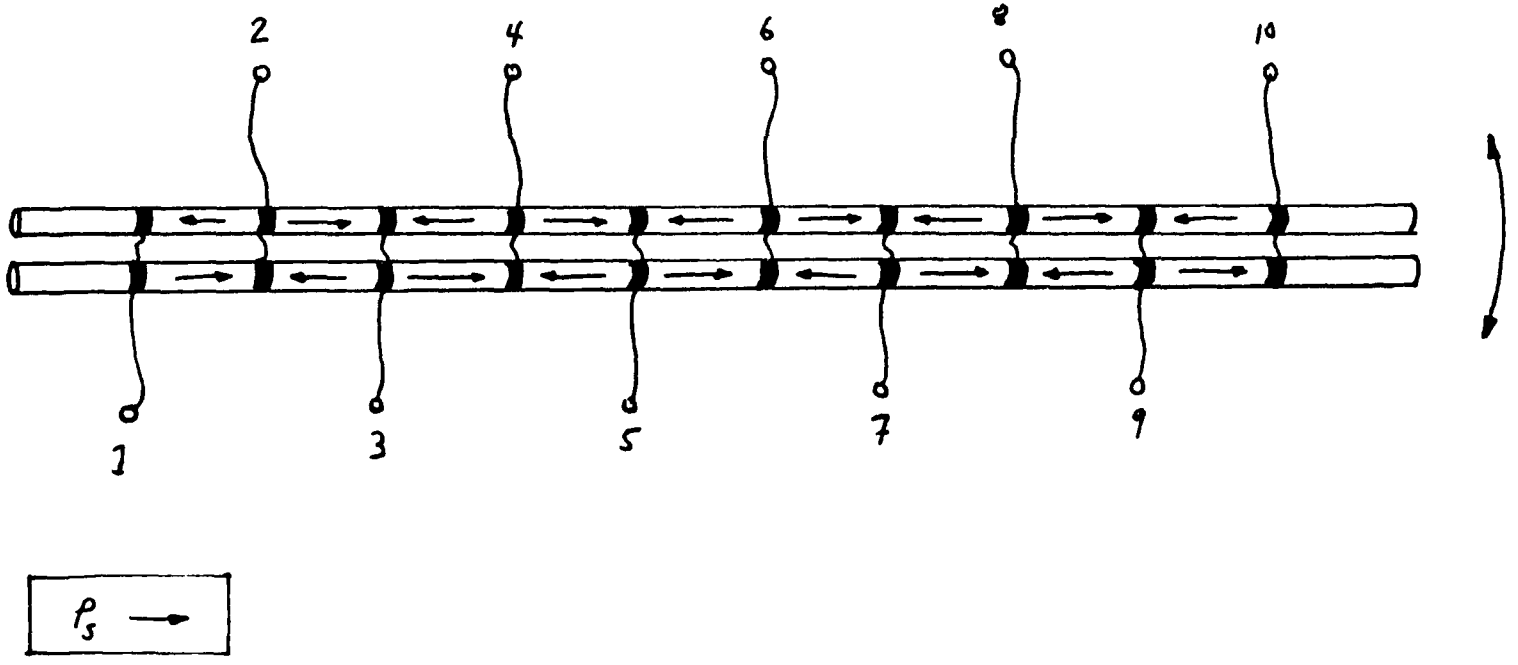


Fig.3 Electrode configuration for resonance measurement.

Fig 4 Electrode configuration for 2-tube modile.



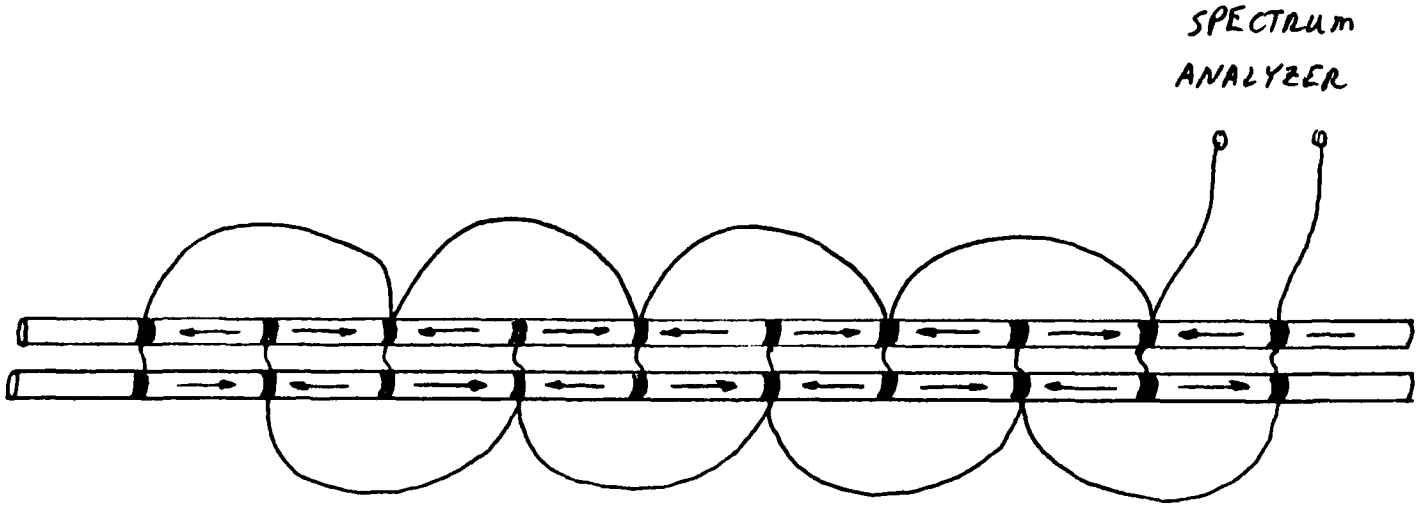


Fig.5 Electrode configuration for k_{eff} measurment.

$$k_{eff} = \sqrt{1 - \frac{3350^2}{3550^2}}$$

$$= 0.33$$

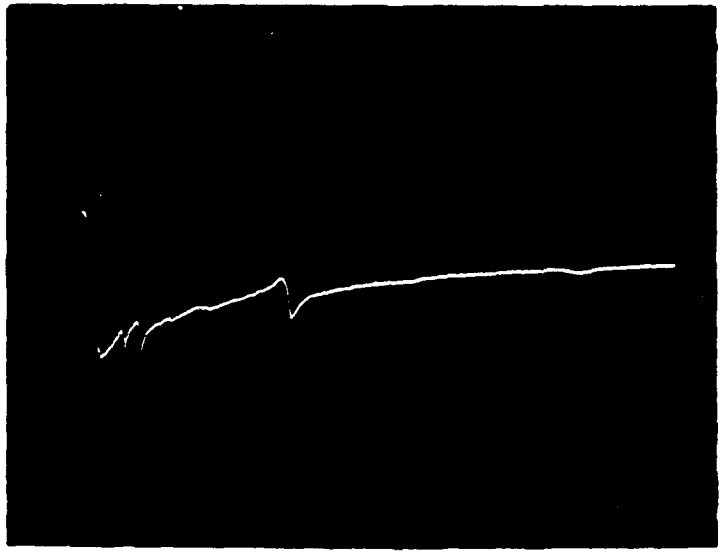


Fig.6 Spectral data for k_{eff} caluculation.

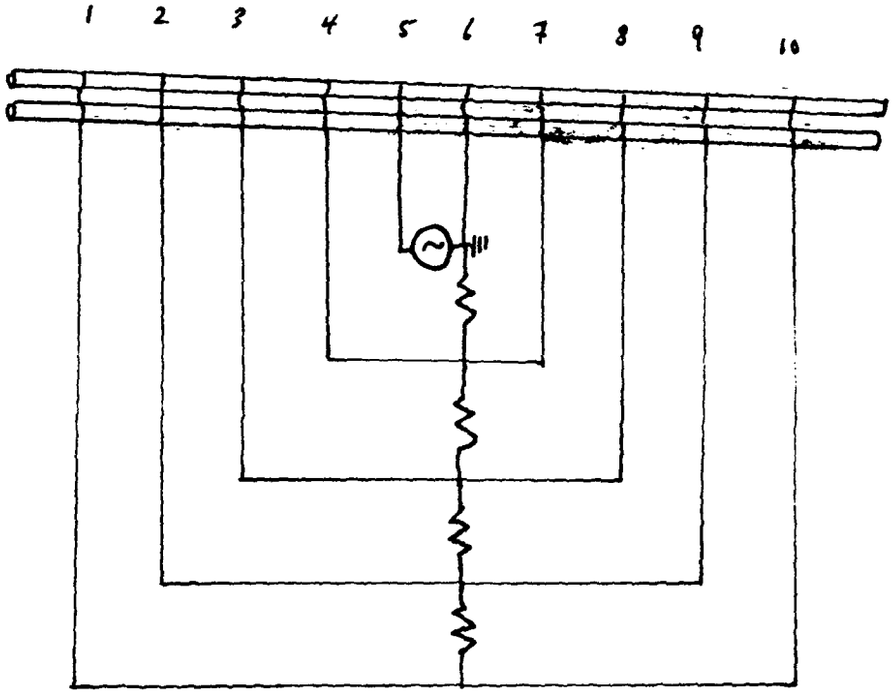
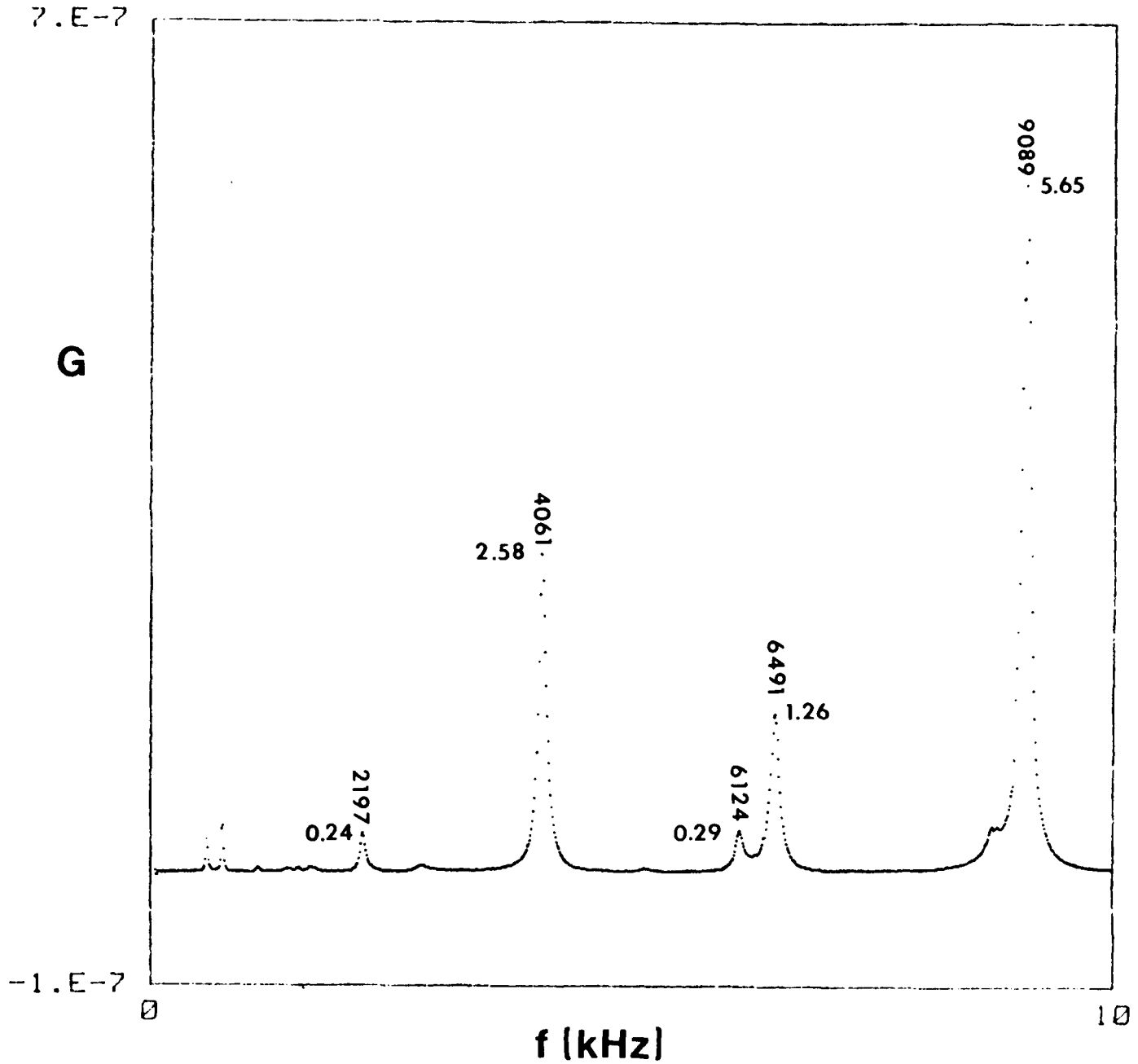


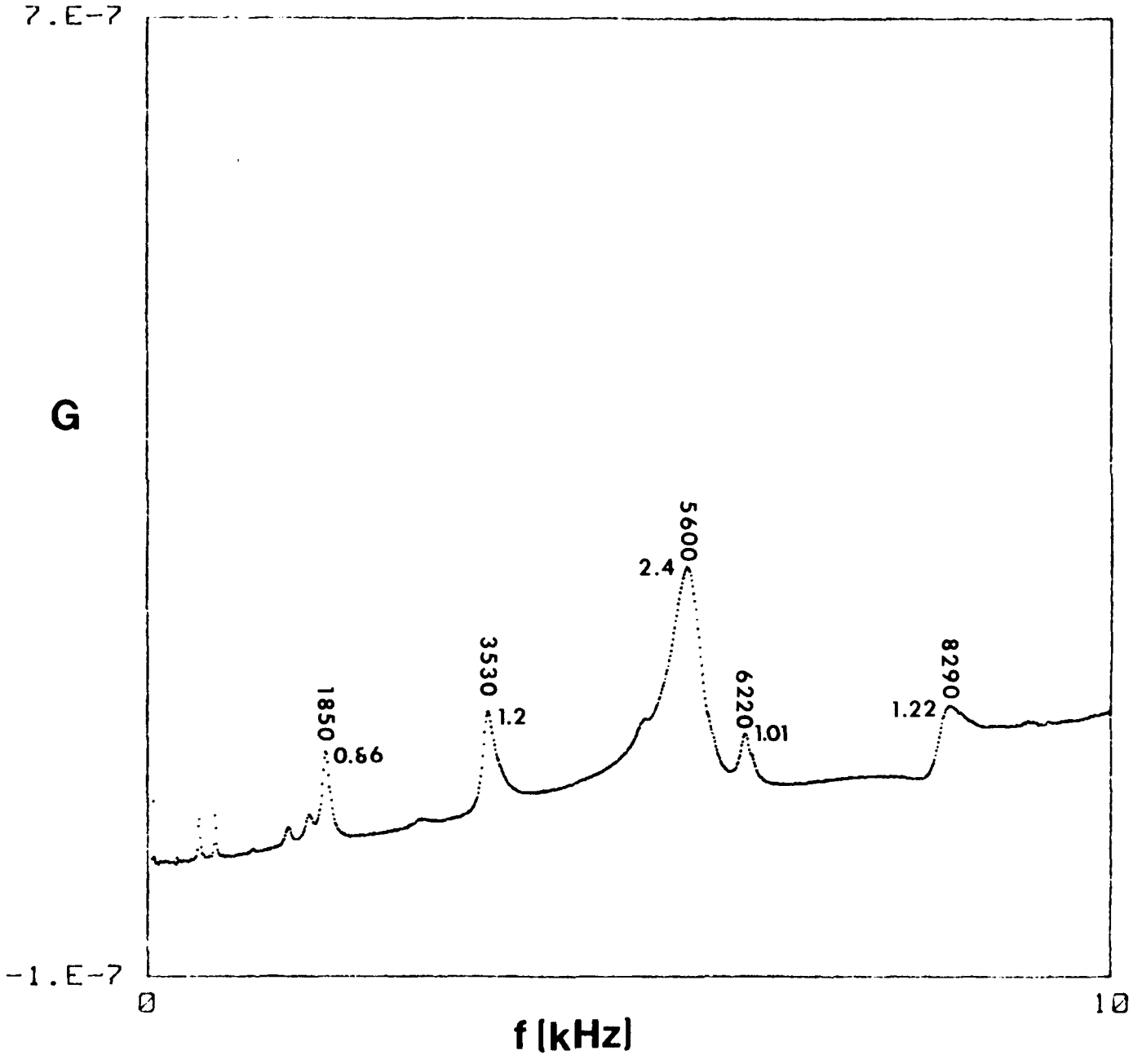
Fig.7 Damping circuit with external resistance.

Fig.8,a



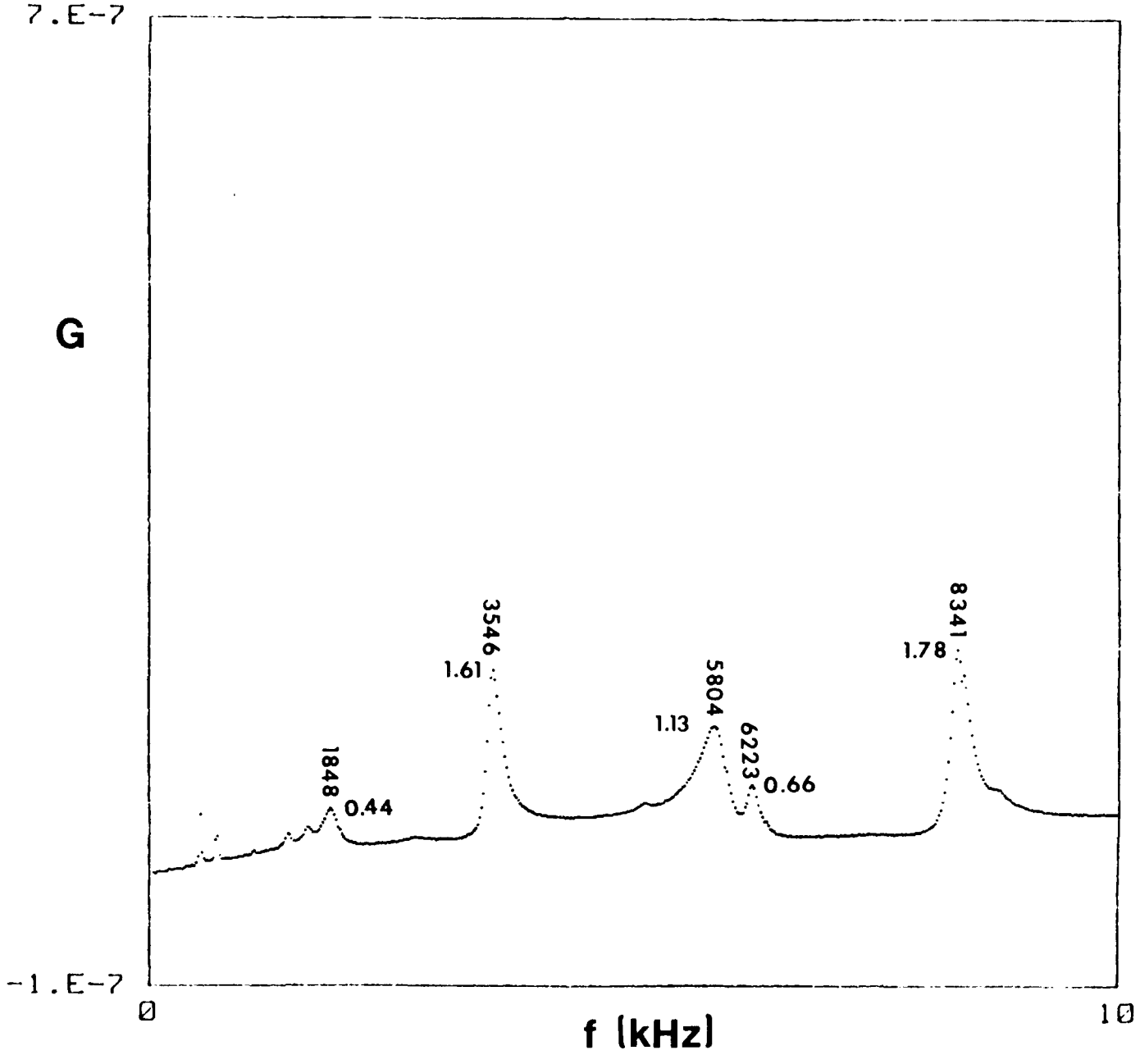
10.5 Hz interval
0.016 rad δ_m

Fig.8,b



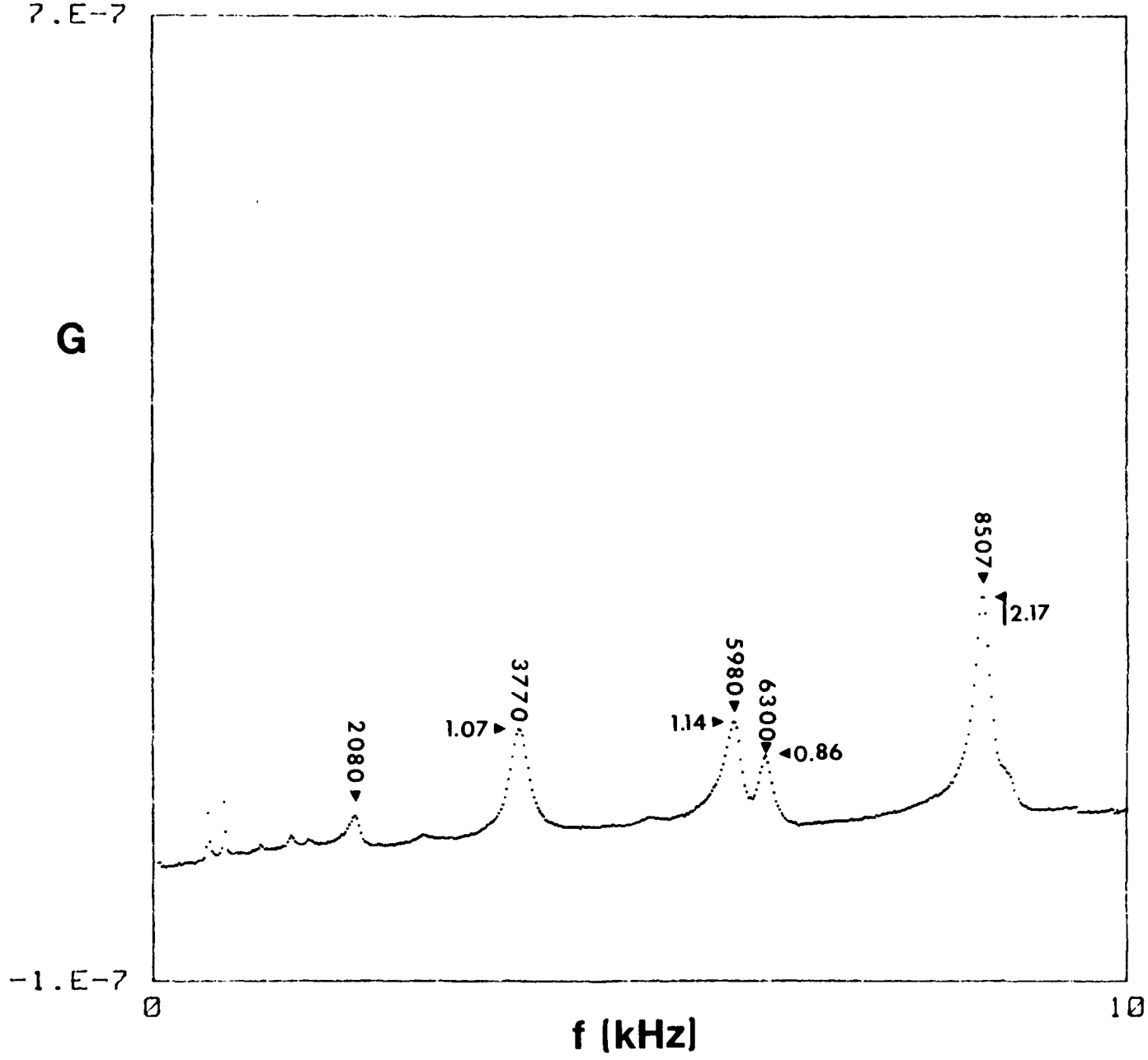
10 Hz interval

Fig.8,c



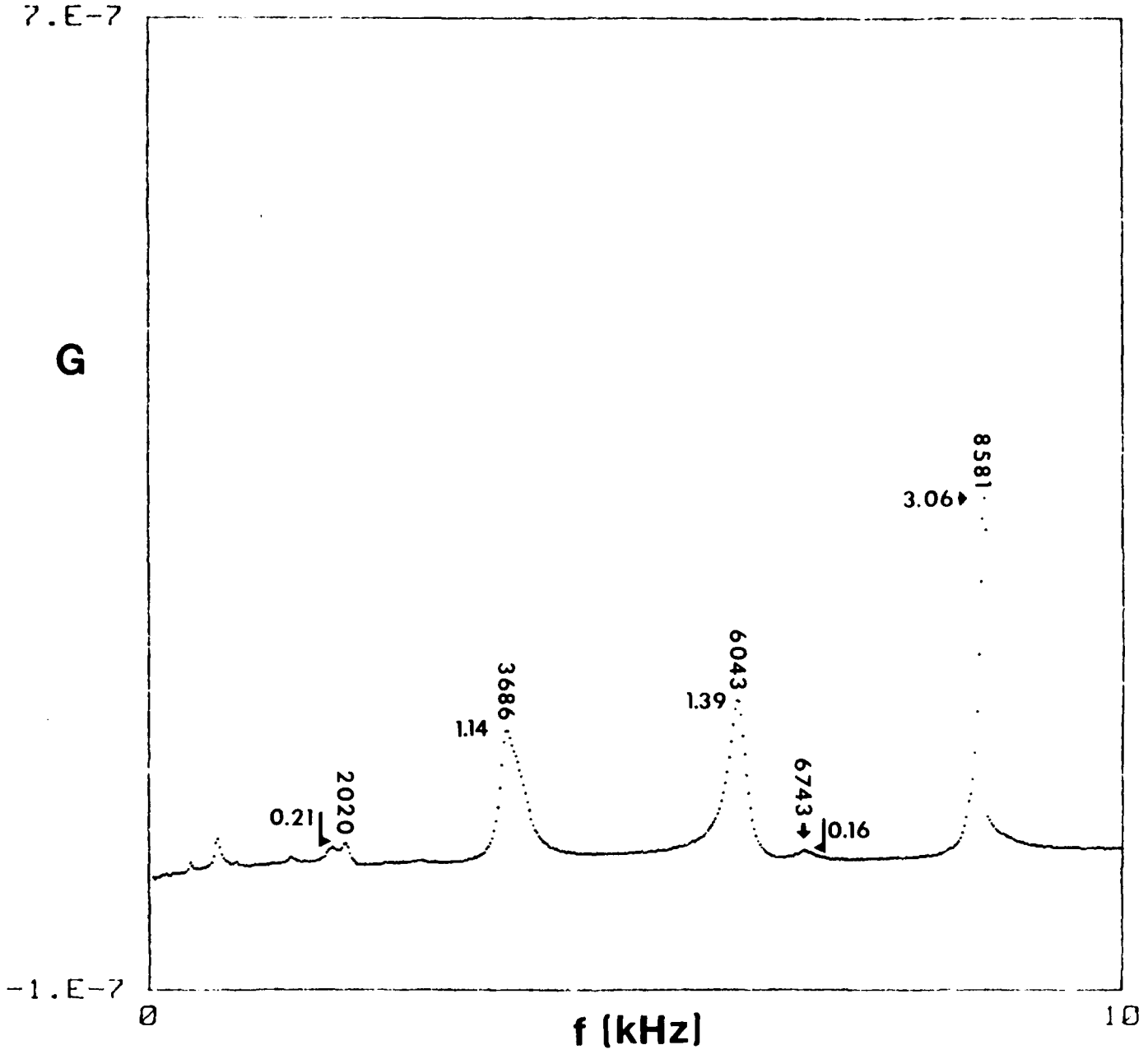
20 Hz interval
0.045 tan δm
4.7 MΩ

Fig.8,d



19.9 = Hz interval
0.06 = Tan δ_m
10 MΩ

Fig. 8e



20 Hz interval
0.07 $Tan\delta_m$
14.7 MΩ

Appendix B

Frequency-Shaped Passive Damping using Resistively-Shunted Piezoceramics

(Proceedings, Conference on Active Materials and Structures, 5-8 Nov.,1991, Alexandria, VA)

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ABSTRACT: The provision of adequate passive damping is an essential aspect of design for practical broadband LTI control of uncertain structural dynamic systems. Resistively-shunted piezoceramics offer potential for significant damping with advantages over more conventional approaches. Tailorable frequency-dependence is especially notable, as damping plays different roles within and beyond the control bandwidth. Guidelines for effective material selection, placement, and shunting are presented in the form of a modified modal strain energy method. Applications to the development of damped structural composite materials are also noted.

1. INTRODUCTION

Vibration damping is essential to the attainment of performance goals for many engineering systems. The ability to tailor frequency-dependence of damping is especially important in practical active structural control applications employing linear, time-invariant compensation. At frequencies above some crossover, robust gain-stabilized performance is attained by assuring, loosely, that modal damping "rolls off" no faster than control authority (Greene and Stein 1979). At frequencies within the control bandwidth, robust broadband phase stabilization of uncertain structural dynamics requires a minimum level of passive damping commensurate with the level of uncertainty (von Flotow and Vos 1991).

The use of piezoelectric materials in combination with resistive and resonant shunting circuits to achieve passive vibration energy dissipation and resonant response reduction has been demonstrated by several researchers, including Hagood and von Flotow (1991). This paper extends earlier work by addressing the use of multiple resistively-shunted piezoceramic elements to achieve specified frequency-dependent damping. Resistive shunting is emphasized because of its relative broadband effectiveness and insensitivity to tuning errors.

Resistively-shunted piezoceramics appear to offer several advantages over more conventional approaches to passive damping. These include: 1) insensitivity of properties to temperature; 2) tailorable frequency-dependent properties; 3) high stiffness; and 4) ability to serve as actuators. *Disadvantages include high density and gradual changes in properties with time.*

2. DAMPING DUE TO ELECTROELASTIC RELAXATION

Piezoelectric materials are potentially effective for damping because of strong coupling between mechanical and electrical behavior: vibratory strains produce potential gradients, and the resulting currents dissipate energy through joule heating in some resistance. Interpretation of the operative physical mechanism as an anelastic relaxation permits the use of classical relations (Nowick and Berry 1972) and the extension of established tools for design purposes.

The electroelastic relaxation strength may be found from consideration of the appropriate material constitutive equations, often specialized to the case of a single non-zero stress. The relaxation strength corresponding to a scalar material modulus, c^E, is given by:

$$\Delta = \frac{e^2}{c^E \varepsilon^S}$$

(Where c^E is a modulus, e a piezoelectric coupling, and ε^S a permittivity; superscript "E" indicates constant field, "S" strain)

This relaxation strength is a measure of the coupling between the displacement and electrical fields. It is related to the square of the electromechanical coupling coefficient, k, another measure often used to describe the properties of such materials. From classical internal friction relations, the corresponding peak material damping loss factor associated with this relaxation, η_{max}, is given by:

$$\eta_{max} = \frac{\Delta}{2(1+\Delta)^{1/2}}$$

Using the complex modulus representation of material properties ($M = M_1 + i\,M_2$), and assuming multiple discrete relaxations, the frequency–dependence of the storage modulus, M_1, the loss modulus, M_2, and the loss factor, η, are given by:

$$M_1(\omega) = M_R\left[1 + \sum_{\text{i relaxations}} \Delta_i \frac{(\omega\tau_{\varepsilon i})^2}{1+(\omega\tau_{\varepsilon i})^2}\right]$$

$\tau_{\varepsilon i}$ is the i^{th} characteristic relaxation time at constant strain and M_R the relaxed (low-freq.) modulus

$$M_2(\omega) = M_R \sum_{\text{i relaxations}} \Delta_i \frac{(\omega\tau_{\varepsilon i})}{1+(\omega\tau_{\varepsilon i})^2}$$

$\tau_{\varepsilon i} = R_i C^S_{tot}$ where R_i is the shunting resistance and C_{tot}^S the total capacitance at constant strain

$$\eta(\omega) = \frac{M_2(\omega)}{M_1(\omega)} = \eta_{max}\frac{2(\omega\bar{\tau})}{1+(\omega\bar{\tau})^2} \quad \text{for a single relaxation} \qquad \text{and } \bar{\tau} = \tau_\varepsilon(1+\Delta)^{1/2}$$

The through-the-thickness capacitance of a single piezoelectric plate is given by:

$$C^S = \frac{A\varepsilon^S}{L}$$

(A is the electrode area, L the thickness)
(C_{tot}^S is twice C^S for two identical capacitors in parallel.)

3. DESIGN GUIDELINES

3.1 Material Properties, Structural Participation, and Frequency–Dependence

The total modal damping of a built-up structure (or composite material) can be estimated as the sum of constituent damping weighted by the relative contribution of each to the total strain energy of the mode. This notion can be extended to the case of resistively-shunted piezoceramics by defining a "coupled strain energy fraction" as follows:

$$V_P^* = \frac{V_P}{U_0 + U_P}$$

U_0 is the strain energy in the base structure;
U_P is the strain energy in the piezoceramic; and
V_P is the effective coupled portion of U_P

For a piezoceramic element bonded to the surface of a bending beam, V_P is given by an expression of the form:

$$V_p = \tfrac{1}{2}(EI)_p \left| \int_{length} \left(\frac{\partial^2 w}{\partial x^2} \right) \left| \frac{\partial^2 w}{\partial x^2} \right| dx \right|$$ (Volume integral of non-positive semidefinite quantity)

Note that it is possible for V_P to be nearly zero even when U_P is not; for example, when a small piezoceramic element is nearly centered on a "strain node," or when the characteristic length of vibration is smaller than the piezo length. This characteristic is closely related to the spatial filtering property of continuously distributed sensors as described in Collins *et al* (1991). The effects of piezoceramic placement on mode shapes and strain energy distribution must also be considered in design, as should the frequency-dependence of material modulus.

The piezoelectric damping added to a structural vibration mode "j" may be considered approximately (for small damping) as the sum of frequency-dependent contributions from each of "i" elements, each with its own relaxation time.

$$\zeta_j(\omega) = \sum_{i\ piezos} \underbrace{\tfrac{1}{2}\eta_{max\,i}}_{material} \underbrace{V^*_{Pj\,i}}_{structural} \underbrace{\frac{2(\omega\bar{\tau}_i)}{1+(\omega\bar{\tau}_i)^2}}_{frequency\ (R)}$$

ζ_j is a **modal damping ratio**, but η_i is a **material damping loss factor.**

3.2 Experimental Validation

The validity of these guidelines were explored using a series of cantilevered beam tests following those described by Hagood and von Flotow (1991). Surface-mounted piezos with transverse coupling (k_{31}) were used (longitudinal strains and transverse voltage gradients).

Figure 1 summarizes the results, which agreed fairly well with theory. Peak damping was slightly less than that predicted using manufacturer-furnished property data, but in good agreement with published results. The discrepancy may be due to material aging, imperfect bond load transfer, or use of baseline mode shape to estimate strain energy distribution. For the material used, the value of k_{31} was approximately 0.35.

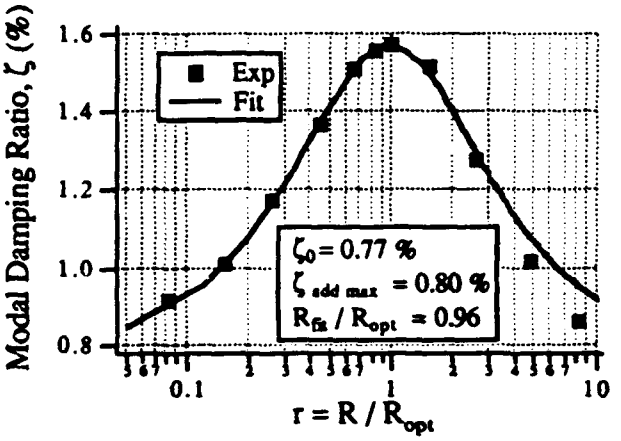

Figure 1: Experimental Results for Single R

3.3 Frequency Shaping

The ability to specify the electroelastic relaxation time through the selection of a shunt resistor is one of the most important features of passive piezoelectric damping. A designer can, by carefully defining a combination of material and structural parameters, tailor the frequency-dependence of damping to suit the requirements of a specific application. Such design variables include the piezoelectric material used (and its constitutive properties); the primary mode of deformation; electrode locations; the amount, shape, placement, and orientation of the piezoelectric material on the structure; and the shunting resistances.

As shown in Figure 2, different kinds of typical material damping behavior can be approximated—however, a designer need not be constrained to duplicate such "classical" behavior. In general, for a fixed amount of piezoelectric material, there is a trade between peak damping and effective frequency range. The design problem is similar to that faced in obtaining a discrete relaxation spectrum from an experimentally-determined material dynamic response function.

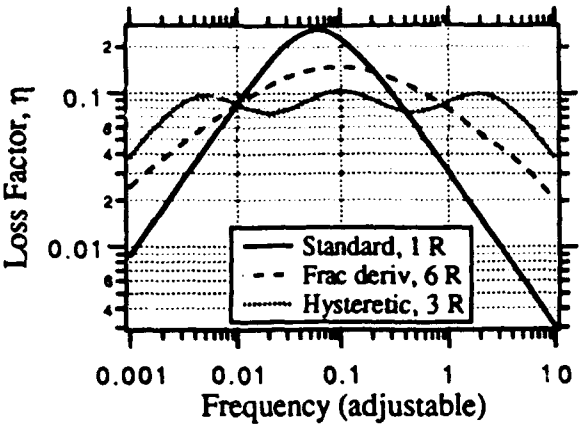

Figure 2: Examples of Tailored Damping

4. POTENTIAL APPLICATIONS TO COMPOSITE MATERIALS

As noted in the preceding, piezo placement has a significant impact on achievable structural modal damping. However, if the elements could be scaled down and proliferated throughout a structure, possibly as reinforcement in a structural composite material, significant material damping could be achieved without sensitivity to placement. Using higher longitudinal 3-3 coupling could result in peak loss factors in excess of 25%, even at low volume fractions.

Basic research in progress at Penn State is addressing the possibility of developing such a composite (Yoshikawa *et al* 1991). Key challenges include the fabrication of piezoceramic whiskers, poling and electroding, and providing an integral, tailorable resistive path. Needs in the area of modeling / optimization may be met through the development of multi-field finite elements (Lesieutre 1992) or network impedance models (Hagood and von Flotow 1991).

5. SUMMARY

Resistively–shunted piezoceramics offer potential for significant damping with advantages over more conventional approaches. A modified modal strain energy method has been developed and tested to guide material selection, placement, and shunting in the pursuit of tailored frequency-dependent damping for structural control applications.

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FREQUENCY-SHAPED PASSIVE DAMPING USING RESISTIVELY-SHUNTED PIEZOCERAMICS

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The use of piezoelectric materials in combination with resistive and resonant shunting circuits to achieve passive vibration energy dissipation and resonant response reduction has been suggested and demonstrated by several researchers. This paper extends earlier work by addressing the use of multiple resistively-shunted piezoceramic elements to achieve specified frequency-dependent damping. Different kinds of typical material damping behavior can be approximated, including and hysteretic and fractional derivative damping. However, a designer need not be constrained to duplicate such "classical" material damping behavior.

The task of developing a collection of resistively-shunted piezoelectric elements to achieve a desired variation of effective material damping with frequency is shown to be similar to the task faced by workers in internal friction in obtaining a relaxation spectrum from an experimentally-determined dynamic response function. However, depending on the specifics of the structure to be damped as well as the dimensions of the piezo-elements relative to the shortest wavelengths of interest, element placement has a significant impact on achievable structural modal damping (as it does for constrained-layer viscoelastic damping treatments).

The paper presents two different strategies for resistively-shunted piezoelectric damping design, one based on a modified modal strain energy method and the other, on an energy dissipation approach. Experimental results obtained using a cantilevered aluminum beam with surface-mounted ceramic patches are described. Implications for, and progress in, engineering structural composite materials with shunted piezoelectric constituents are also discussed.

Sol-gel processing of $PbTiO_3$ and $Pb(Zr_{0.52}Ti_{0.48})O_3$ fibers

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Homogeneous and stoichiometric $PbTiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$ gel fibers were drawn from viscous solutions prepared by sol-gel processing of alkoxide precursors. The fibrous gels on heating at 450 and 600 °C, respectively, formed the well-crystallized phases of $PbTiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$. Fibers heat treated at 700 °C are a few centimeters long and 50 to 150 μm in diameter. $PbZr_{0.52}Ti_{0.48}O_3$ fibers subjected to heat treatment at 700 °C for 1 h consisted of fully dense submicron grains (0.15 to 0.2 μm). However, $PbTiO_3$ fibers under analogous conditions showed a few micropores with grains of ~0.1 μm. Dielectric constants of these $PbTiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$ fibers were approximately 300 and 800, respectively.

I. INTRODUCTION

The sol-gel process with metal alkoxides as precursors has been extensively studied for the fabrication of ceramic materials of various forms such as ultrafine powders, sintered bodies, thin films, and fibers.[1–4] Also, this technique allows the preparation of some materials that are difficult to be synthesized by conventional ceramic method. Metal alkoxides, M(OR)n (where M and R represent metal ions and alkyl groups, respectively) through hydrolysis and polycondensation reactions form gels, which are converted to ceramic materials by heat treatment at lower processing temperatures. The formation of gel fibers requires linear or chain-like polymerization of alkoxide solutions.[5] This can be achieved by adding a relatively small amount of water and concentrating the polymerized alkoxide solutions. When concentrating these solutions the volatile products are eliminated, which further controls the condensation-polymerization sequence. In addition, fiber drawing from these concentrated solutions leads to a rapid increase in surface area/volume ratio, resulting in further evaporation of any remaining volatile components. By following this procedure, a number of sol-gel fibers of SiO_2,[6] Al_2O_3,[7] TiO_2,[5] ZrO_2,[8] $LiNbO_3$,[9] $PbTiO_3$,[10] and $YBa_2Cu_3O_{7-x}$[11] have been prepared.

$PbTiO_3$ (PT) and $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) are perovskite-type ferroelectric materials with potential applications in surface acoustic wave devices, pyroelectric type sensors, and supersonic wave probes for biomedical imaging.[12] PT has a Curie temperature (T_C) at about 490 °C, a large tetragonality ($c/a = 1.06$), a large spontaneous polarization (75 $\mu C/cm^2$), and a relatively small dielectric constant (~350).[13] $Pb(Zr_xTi_{1-x})O_3$, on the other hand, has a pronounced maximum in dielectric constant (~800) close to the morphotrophic phase boundary (x = 0.52 to 0.55).[12,14] Furthermore, PZT has a large pyroelectric response, large electromechanical coupling coefficient, large electro-optic effect, and a large spontaneous polarization. Accurately controlled microstructures and special shaping by chemical processes like the sol-gel technique are essential for obtaining dense PT and PZT ceramics for high-performance applications. The sol-gel ceramic materials of PT and PZT in the fibrous form may exhibit increased responsivity in small-scale devices. Also, PZT fiber-polymer composites can be used in passive vibrational damping and as transducers with certain advantages over the single phase ceramics.

Because of the volatility of lead at processing temperatures, PT and PZT fibers cannot be fabricated by the melt process in the same way as silica fibers. The following chemical processes have therefore been attempted to prepare PT and PZT fibers. Nishi *et al.*[15] reported the formation of $PbTiO_3$ fibers (1 to 10 μm in diameter and 20 to 100 μm in length) by hydrothermal reactions between $Pb_2O(OH)_2$ and $2K_2O \cdot 11TiO_2 \cdot 3H_2O$ or $TiO_2 \cdot nH_2O$ fibers in the presence of aqueous KOH. Thick $PbTiO_3$ fibers of ~500 μm in diameter were extruded by Del Olmo and Calzada[16] from a fresh inorganic $TiO(OH)_2/1/2Pb_2O(OH)_2$ gel with appropriate rheological characteristics. Walter *et al.*[17] prepared PZT fibers by impregnation of PZT precursor solution into activated carbon-fiber templates. The PZT fibers of identical morphology as the template material were obtained by burning out the carbon. However, the fibers obtained by this method were found to be porous and required higher temperatures for densification. This paper reports the fabrication of PT and PZT fibers from viscous spinnable solutions prepared by sol-gel processing of alkoxide precursors.

II. EXPERIMENTAL

The scheme for the preparation of PT and PZT gel fibers is outlined in Fig. 1. Lead acetate tri-

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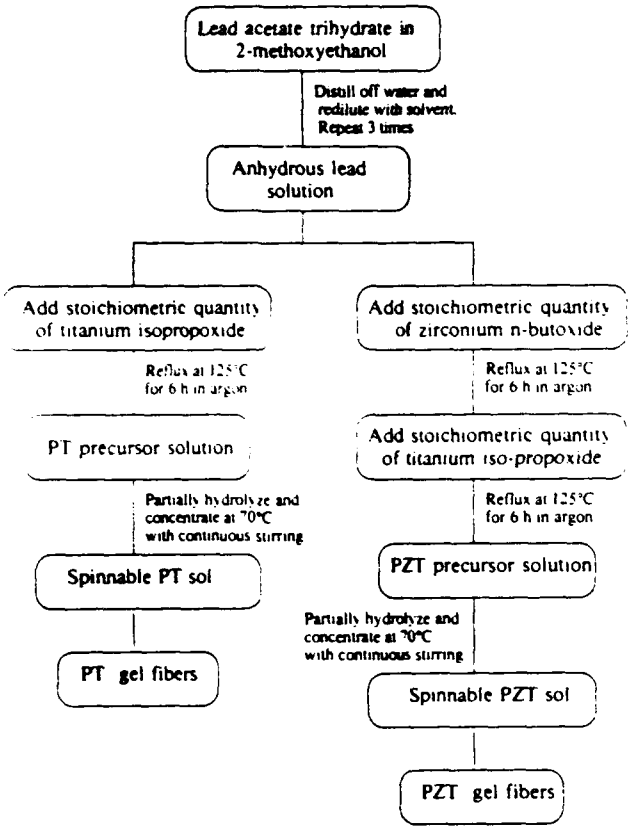


FIG. 1. Scheme for the preparation of $PbTiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$ fibers by a sol-gel process.

hydrate [$Pb(CH_3COO)_2 \cdot 3H_2O$], zirconium n-butoxide, [$Zr(OBu)_4$], 80% solution in 1-butanol and titanium isopropoxide [$Ti(OPr')_4$] obtained from Aldrich Chemical Company were used as the starting materials. PT precursor solution was prepared from $Pb(CH_3COO)_2 \cdot 3H_2O$ and $Ti(OPr')_4$, according to the procedure originally reported by Blum and Gurkovich.[18] $Pb(CH_3COO)_2 \cdot 3H_2O$ (0.2 M) was dissolved in 6 M 2-methoxyethanol. Water was removed from $Pb(CH_3COO)_2 \cdot 3H_2O$ by repeated distillations (three times) in 2-methoxyethanol under argon. After distillation, 2-methoxyethanol was added to the solution to maintain the initial lead/2-methoxyethanol ratio. To this solution, a stoichiometric quantity of $Ti(OPr')_4$ was added and refluxed at 125 °C for ~6 h to form the PT precursor. PZT precursor solution of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ was prepared from $Pb(CH_3COO)_2 \cdot 3H_2O$, $Zr(OBu)_4$ and $Ti(OPr')_4$. After the dehydration of $Pb(CH_3COO)_2 \cdot 3H_2O$ by the above procedure, a stoichiometric quantity of $Zr(OBu)_4$ was added to the lead solution and refluxed at 125 °C for ~6 h. $Ti(OPr')_4$ was then added to the Pb–Zr solution and again refluxed at 125 °C for ~6 h to form the PZT precursor solution.

A solution of 0.1 ml of water diluted in 5 ml of 2-methoxyethanol was added to a vigorously stirred 0.02 M PT or PZT precursor solution containing 0.1 ml conc. HNO_3. The solution was concentrated by stirring at ~70 °C, to form a viscous sol. The spinnability of the sol was examined by dipping a glass rod into the sol and pulling it up. Gel fibers of a few centimeters long were drawn from the spinnable sol. The gel fibers were dried at room temperature for 12 h and slowly heated to 700 °C at a heating rate of 1 °C/min.

Phase transformations and the weight loss of the fibrous PT and PZT gels obtained from the spinnable sol were studied using Perkin-Elmer differential thermal (Model DTA 1700) and thermogravimetric (Delta Series TGA7) analyzers interfaced with a computerized data acquisition and manipulation system. Phases crystallizing in the heat-treated samples were identified using a Scintag (Model DMC 105) diffractometer with Ni filtered Cu K_α radiation. The microstructure and the diameter of the heat-treated fibers were studied by a scanning electron microscope (SEM), ISI-DS 130, Akashi Beam Technology Corporation, Japan. For SEM studies the fibers were etched with 1% HCl in water for 2 min.

The dielectric constants of single fibers of PT and PZT were obtained using a precision capacitance bridge (Model GR 1621, General Radio, MA). Capacitance was obtained using a three terminal shielded measurement at 1 kHz. The test fixture capacitance was compensated by open circuit subtraction. Fibers of 1 to 2 mm in length were attached to sputtered gold electrode pads using silver paint.

III. RESULTS AND DISCUSSION

Figure 2 shows the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves for the fibrous PT gel previously dried for 12 h at room temperature and heat treated at 300 °C for 1 day to remove the organics and carbon. From the TGA curve it can be seen that the gel exhibited ~3% weight loss when heated from 50 to 700 °C due to the presence of residual carbon. Removal of organics and the major amount of carbon from the fibrous gel by heat treating at 300 °C for 1 day provided unambiguous assignments of the peaks in DTA at 380 and 485 °C to the crystallization of PT and its transformation from tetragonal to a distorted cubic phase.[19]

XRD patterns of the fibrous PT gel heat treated at 400 and 450 °C for 3 h and 1 h, respectively, are shown in Fig. 3. The gel heated at 300 °C for 1 day was x-ray amorphous. Well-crystallized peaks corresponding to stoichiometric tetragonal PT are observed for the sample heat treated at 450 °C. Blum and Gurkovich,[18] in contrast, observed the formation of crystalline PbO in addition to PT in the heat-treated alkoxide-derived PT gel. The formation of $PbTi_2O_5$ as a second phase was observed in the films prepared from equimolar

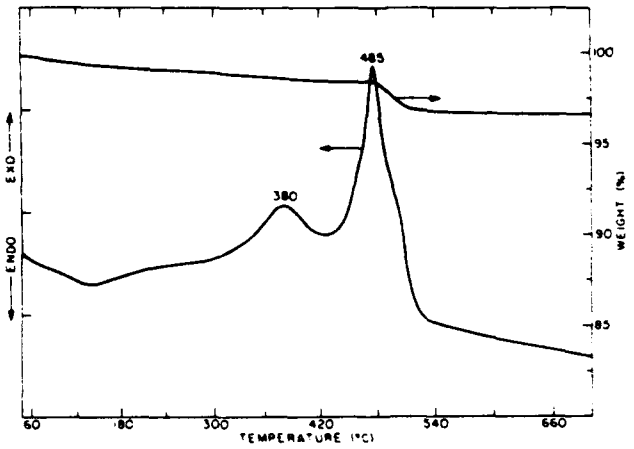


FIG. 2. DTA and TGA curves for the fibrous $PbTiO_3$ gel preheated to 300 °C for 24 h.

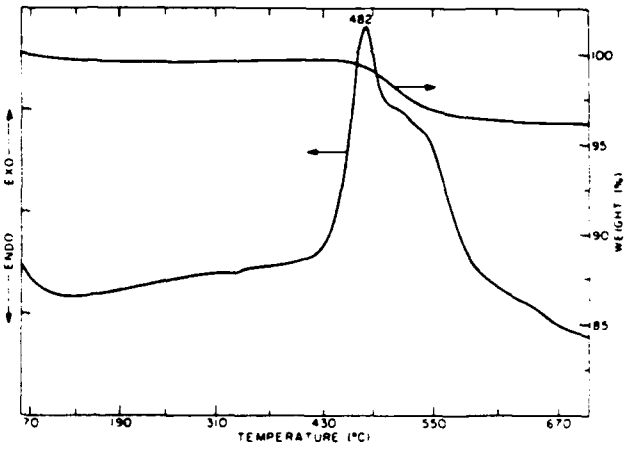


FIG. 4. DTA and TGA curves for the fibrous $PbZr_{0.52}Ti_{0.48}O_3$ gel preheated to 300 °C for 24 h.

Pb–Ti alkoxide solution, and heat treated at temperatures in excess of 570 °C.[20,21] This was attributed to the evaporation of lead during heating. The formation of well-crystallized, stoichiometric PT from the fibrous gel at a temperature as low as 450 °C in the present investigation indicates the highly homogeneous nature of the spinnable sol precursor.

Figure 4 shows DTA and TGA curves for PZT fibrous gel previously heat treated at 400 °C for 24 h. As observed for PT gel, the preheated PZT gel also exhibited a weight loss of ~3% in the temperature range of 50 to 700 °C. The gel exhibited a sharp exotherm at 482 °C, followed by a shoulder at 530 °C in DTA. These peaks c... be attributed to the crystallization of a pyrochlore phase and its conversion into perovskite PZT. XRD results of the fibrous PZT gel heat treated at 500 °C for different durations indicated the formation of pyrochlore and perovskite phases, while heat treatment at 600 °C resulted in only the perovskite phase (Fig. 5).

SEM micrographs of PT and PZT fibers heat treated at 700 °C for 2 and 1 h, respectively, and etched with 1% HCl are shown in Figs. 6 and 7. The fibers obtained were of the order of 50 to 150 μm in diameter. Typical PT and PZT fibers are shown in Figs. 6(a) and 7(a). Under higher magnification, these fibers exhibited fine grains: ~0.1 μm for PT and 0.15 to 0.2 μm for PZT. The observed microstructures clearly reveal the formation of dense polycrystalline ceramic in the case of PZT; however, PT fiber exhibited a few micropores. As observed by many investigators, PT is less prone to sintering without additives such as lanthanum.

The dielectric constants of PT and PZT fibers were found to be approximately 300 and 800, respectively. The corresponding loss values (tan δ) for these fibers

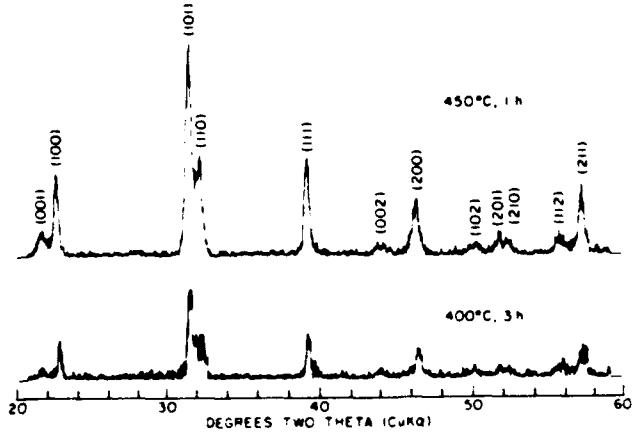


FIG. 3. XRD patterns for the fibrous $PbTiO_3$ gel heat treated at 400 and 450 °C for 3 and 1 h, respectively.

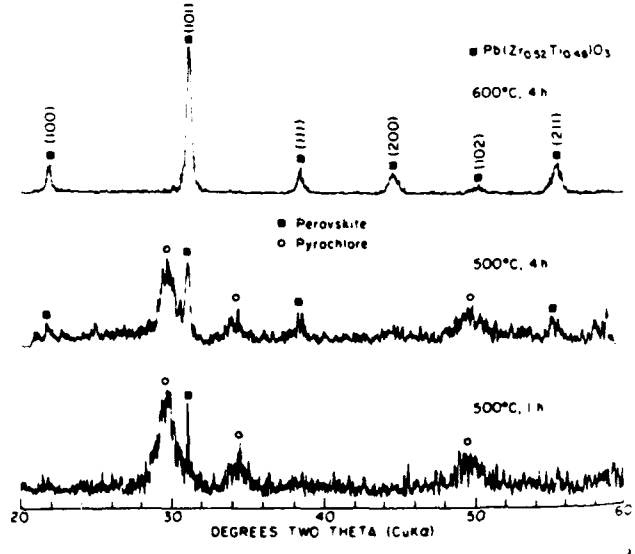
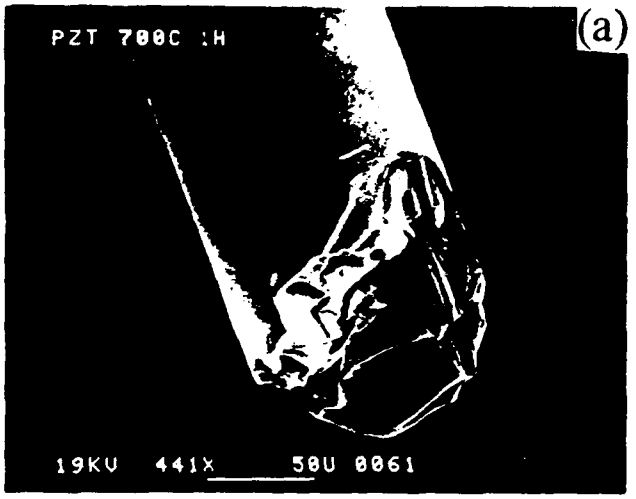


FIG. 5. XRD patterns for the fibrous $PbZr_{0.52}Ti_{0.48}O_3$ gel heat treated at different temperatures.



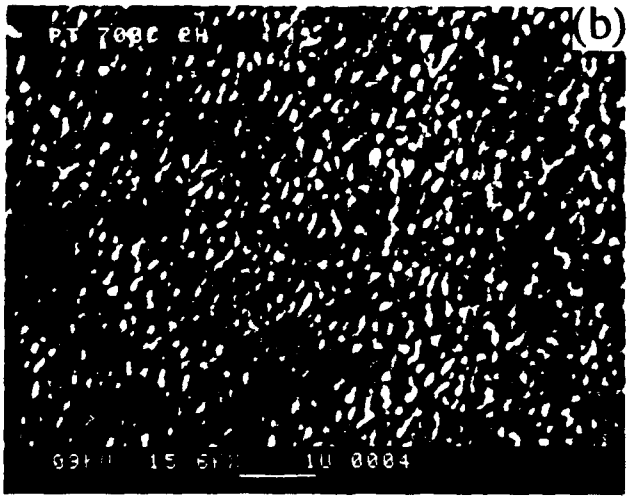


FIG 6. SEM micrographs of $PbTiO_3$ fibers heat treated at 700 °C for 2 h and etched in 1% HCl for 2 min. (b) is a higher magnification of (a).

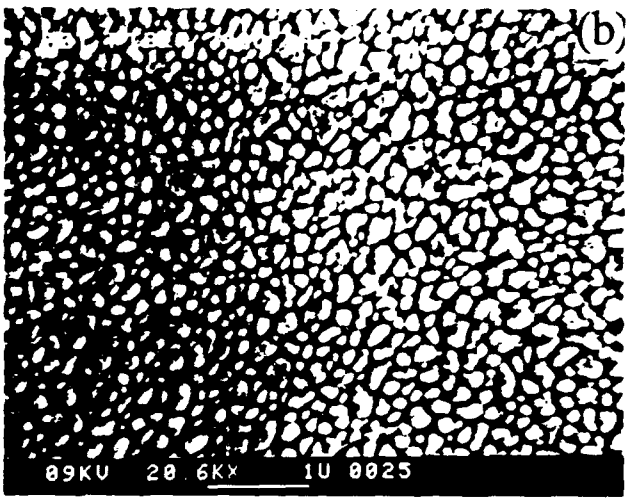


FIG 7. SEM micrographs of $PbZr_{0.52}Ti_{0.48}O_3$ fibers heat treated at 700 °C for 1 h and etched in 1% HCl for 2 min. (b) is a higher magnification of (a).

were of the order of 0.06 to 0.08. These values are in agreement with those reported for sol-gel derived thin films of the same composition.[13,14] Studies are now being carried out to improve the sinterability of PT fibers by incorporation of suitable additives and to assess the PZT fiber embedded in polymer matrix for the passive vibrational damping studies.

IV. CONCLUSIONS

Spinnable viscous sols of $PbTiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$ were obtained by controlling the hydrolysis and polycondensation reactions of alkoxide precursors. Uniform gel fibers were drawn from the spinnable sols. The fibrous gels yielded well-crystallized $PbTiO_3$ and $PbZr_{0.52}Ti_{0.48}O_3$ at 450 and 600 °C, respectively. $PbZr_{0.52}Ti_{0.48}O_3$ fibers fired at 700 °C for 1 h were found to be fully dense with submicron (0.15 to 0.2 μm) grains, while the $PbTiO_3$ fibers fired at 700 °C for 2 h were microporous with grains of ~0.1 μm. The measured dielectric properties agreed well with the corresponding sol-gel derived thin films.

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ABSTRACT for ASM International Materials Week '91
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PASSIVE PIEZOELECTRIC DAMPING COMPOSITES

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Many modern engineered structures make use of high tech composites or intermetallics which have limited damping properties. The presently available solution of attaching thin layers of polymeric damping materials is limiting and has led to a search for a more effective means of damping. In this work, we have investigated the possible use of piezoelectric materials with large electromechanical energy conversion coefficients (i.e., large coupling coefficients) for passive damping applications. In order to attenuate mechanical vibrations in a passive absorbing element, it is essential to convert a major fraction of mechanical/elastic energy into heat. The idea behind passive piezoelectric vibration damping is to efficiently convert a large fraction of elastic energy into electrical energy using the large piezoelectric coupling coefficient of ferroelectric ceramics. The electrical energy is then dissipated as heat using resistive coating on the ceramic element.

Piezoelectric ceramics of the $PbZrO_3$-$PbTiO_3$ (PZT) solid solution system were used as the piezoelectric element in our passive damping composite materials because of their superior piezoelectric properties which include: 1) extremely large piezoelectric coefficients and coupling factors; 2) a high Curie temperature (~350°C) permitting use at higher temperatures; 3) a high elastic modulus; and 4) the ability to further tailor the properties of PZT ceramics by compositional modifications.

A stack of ceramic PZT disks shunted by optimally tuned resistors was constructed for damping of the 3-3 mode vibration using an electrical resonance technique. It gave a maximum mechanical loss (tan δm) of 0.25 with an elastic modulus of 70 to 90 GPa. This demonstrates that high damping can be achieved with piezoelectric ceramic composites without sacrifice of strength and rigidity.

To investigate the incorporation of these piezoelectric-resistive composite damping elements directly into high strength fiber reinforced composites we have investigated small diameter cylinders of PZT as well as PZT-coated glass fibers. An analysis of the damping properties of such fibers appropriately coated with layers of optimum resistivity and embedded in polymer to 50 vol.% loading has been carried out. The results indicate that specific damping capacity of more than 6% can be achieved in the low frequency range while maintaining an elastic modulus of 70 GPa. Experimental results of fine PZT tubes embedded in polymer matrix will also be presented.